Macromolecules 1987, *20*, 1196–1199

(18) Fritz, J. S.; Moyers, E. M. *Talanta* **1976**, *23*, 590.

(19) Yeh, H. C.; Eichinger, B. E.; Anderson, N. H. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2575.

(20) Blasius, E.; Janzen, K. P. *Isr. J. Chem.* **1985**, *26*, 25.

(21) Sekine, T.; Hasegawa, Y. *Solvent Extraction Chemistry*; Marcel Dekker: New York, 1977; p 464.

(22) Alexandratos, S. D.; Quillen, D. R.; McDowell, W. J. *Sep. Sci. Technol.* **1987**, *22*, 983.

(23) Roche, T. S.; Wilkins, R. G. *Chem. Commun.* **1970**, 1681.

(24) Kielland, J. German Patent 715 200, 1941.

(25) Bayer, E.; Fiedler, H.; Hock, K. L.; Otterbach, D.; Schenk, G.; Voelter, W. *Angew. Chem.* **1964**, *76*, 76.

(26) Sugil, A.; Ogawa, N.; Hashizume, H. *Talanta* **1980**, *27*, 627.

(27) Takagi, M.; Ueno, K. In *Top. Curr. Chem.* **1984**, *121*.

(28) Agett, J.; Udy, D. J. *J. Inorg. Chem.* **1970**, *32*, 2802.

(29) Harmon, H. D.; Peterson, J. R.; McDowell, W. J.; Coleman, C. F. *J. Inorg. Nucl. Chem.* **1976**, *38*, 155.

(30) Antikainene, P. J.; Dyrssen, D. *Acta Chem. Scand.* **1960**, *14*, 86.

(31) Mathur, J. N. *Solvent Extr. Ion Exch.* **1983**, *1*, 349.

(32) Choppin, G. R. *Sep. Sci. Technol.* **1981**, *16*, 1113.

(33) Alexandratos, S. D.; Painton, C. D. C.; Quillen, D. R.; McDowell, W. J. *Sep. Sci. Technol.*, submitted.

(34) Farrall, M. J.; Frechet, J. M. J. *J. Org. Chem.* **1976**, *41*, 3877.

(35) Millar, J. R. In *Mass Transfer and Kinetics of Ion Exchange*; Liberti, L, Helfferich, F. G., Eds.; Martinus Nijhoff: The Hague, 1983; Chapter 1.

(36) Green, B. R.; Hancock, R. D. *Hydrometallurgy* **1981**, *6*, 353.

(37) Barrett, J. H. U.S. Patent 3 843 566, 1974.

(38) Clay, J. P. *J. Org. Chem.* **1951**, *16*, 892.

(39) Kinnear, A. M.; Perren, E. A. *J. Chem. Soc.* **1952**, 3437.

(40) Alexandratos, S. D.; Strand, M. A.; Quillen, D. R.; Walder, A. J. *Macromolecules* **1985**, *18*, 829.

(41) Peppard, D. F.; Mason, G. W.; Andrejasich, C. M. *J. Inorg. Nucl. Chem.* **1965**, *27*, 697.

(42) Alexandratos, S. D.; Wilson, D. L.; Strand, M. A.; Quillen, D. R.; Walder, A. J.; McDowell, W. J. *Macromolecules* **1985**, *18*, 835.

Cis–Trans Isomerization of Alkyl-Substituted Allylic Ion Pairs. 2. Isomerization of Oligobutadienyllithium and Oligobutadienylsodium and of *n*-Butylallylpotassium and Its Relation to Anionic Butadiene Polymerization in Tetrahydrofuran

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Received August 21, 1986

ABSTRACT: The allylic active centers present in the anionic polymerization of dienes exist in cis and trans forms. In THF the cis form is the more stable but is not normally formed in the transition state. Measurements of trans → cis isomerization rates are required to adequately describe the mechanism. These have been determined for oligobutadienyllithium and -sodium and for *n*-butylallylpotassium over a temperature range. The order of rates is Li $\gg$ Na $>$ K as previously observed for neopentylallyl compounds. A bulky end-group effect was found important mainly for lithium. The results are correlated with changes of microstructure of polybutadiene observed as a function of temperature and counterion.

Anionic polymerization of dienes in polar or nonpolar solvents proceeds via active centers which can exist in either cis or trans form. The geometrical isomer immediately formed in the transition state is normally not the thermodynamically stable one. Competition between monomer addition and relaxation to the stable form determines which isomer reacts with monomer and influences the reactivity and stereospecificity of the reaction.[1] It is, therefore, important to measure anion-pair isomerization rates in order to fully understand the polymerization mechanism. In a recent publication,[2] we presented data on the trans to cis isomerization rates in tetrahydrofuran of a series of neopentylallyl–alkali metal salts with counterions, lithium, sodium, and potassium. These compounds which are easily prepared have been extensively characterized by spectroscopic techniques[3] and used as models for the growing active centers in anionic polymerization. The presence of a neopentyl substituent on the allylic system may, due to its bulky nature, affect some properties of such systems. There is no evidence that it affects significantly the equilibrium cis/trans ratio; this appears to require the *tert*-butyl group to be directly substituted on the allylic system.[4] A difference in cis,trans isomerization rates between 2-methylneopentylallyllithium and oligomers formed by isoprene addition to it was however observed in the first measured rates of isomerization of an aliphatic allylic compound in heptane.[5] It is important, therefore, to investigate end-group effects on isomerization rates in tetrahydrofuran, particularly if these results are to be used in the interpretation of microstructure changes in anionic polymerization.

Experimental Section

The preparation of suitable lithium compounds can be easily achieved by modification of the standard preparation of neopentylallyllithium.[2,6] Instead of equimolar amounts of butadiene and *tert*-butyllithium, a 3–4-fold excess of butadiene was used in benzene as solvent. The *tert*-butyllithium concentration used was $\sim 10^{-2}$ M, so that the microstructure of the enchained butadiene units will be largely, 1,4.[7] The benzene was removed in vacuum by freeze-drying and the product dissolved in tetrahydrofuran (THF) at $\sim$-90 to -95 °C.

For comparison purposes between the present experiments and those carried out earlier on neopentylallyllithium, the preparation of *n*-pentylallyllithium was attempted. Due to the much slower initiation rate, it cannot be prepared from equivalent amounts of *n*-butyllithium and butadiene. An 80% (mol) yield, however, together with 20% higher molecular weight products (mostly dimer) was obtained from $\sim 10^{-2}$ mol of *n*-butyllithium and a quarter of the number of moles of butadiene in $\sim$10 mL of benzene. The butadiene was distilled slowly from a side arm held at $\sim$-35 °C to a well-stirred solution of the initiator cooled to 5 °C.

A suitable allylic sodium compound could be made by starting with neopentylallylsodium prepared from neopentylallyllithium as described previously.[2] Addition of about 3 mol equiv of butadiene at low temperature in THF would produce a compound with a less bulky substituent on the allylsodium and primarily in the trans form.[9] Suggestions[10] that the small amount of residual lithium compounds present could have some effect on rates of similar processes led us to attempt a direct metalation of

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Table I
Observed Overall Rate Constants (s^{-1}) for Isomerization of Allylic Lithium, Sodium, and Potassium Salts in Tetrahydrofuran

Li	T, °C	–60.9	–62.6	–65.0	–66.0	–68.8	–75.0	–76.6[a]	–85.8	–87.7
	10^4k_{obsd}	42.0	32.0	18.0	16.6	10.0	3.8	3.1	0.57	0.43
Na	T, °C	–26.6	–34.5	–35.7	–36.3	–40.4	–44.1	–52.0	–56.0	
	10^4k_{obsd}	34.3	10.9	15.3	8.3[b]	5.8	4.6[b]	7.7	5.0	
K	T, °C	+13.1	+12.5	+6.5	–1.5	–1.5	–11.2	–16.5		
	10^4k_{obsd}	5.5	6.4	3.1	1.4	1.0	0.30	0.15		

[a] Lithium tetraphenylboride present. [b] ±0.5.

trans-2-heptene by trimethylsilylmethylsodium in THF. Prepared in the same way as the analogous potassium compound,[2] it was, however, found to be considerably less reactive than the latter. No reaction was observed at 10 °C (^{1}H NMR), the spectrum being, after 90 min, identical with that of *trans*-2-heptene plus (trimethylsilyl)methylsodium (δ_{CH_3} –0.18; δ_{CH_2} –2.22). Some metalation did occur after ~40 min at 35 °C, since these signals disappeared, but only weak signals of *cis*-*n*-butylallylsodium could be recognized. The spectral complexity suggested that other reactions were occurring, presumably attack on THF.

Butylsodium prepared from dibutylmercury in the same manner was more reactive, producing a reasonable rate of metalation in THF at –20 °C. The characteristic $CH_2(Na)$ triplet (δ –1.05, J = 8.3 Hz) of butylsodium decreased with a half-life of about 1 h. Characteristic signals from allylic positions (α, β, γ)[2] of *n*-butylallylsodium appeared, e.g., δ 2.60, doublet of triplets, $J_{\beta\gamma}$ = 8.6, $J_{\gamma\delta}$ = 5.2 Hz (cis γ), δ 3.35, doublet of triplets, $J_{\beta\gamma}$ = 13.2, $J_{\gamma\delta}$ = 6.4 Hz (trans γ); δ 6.24, multiplet, $J_{\beta\gamma}$ ~ 9, $J_{\alpha\beta}$ = 10.5 Hz (cis β). Signals characteristic of *trans*-2-heptene at 5.35, 1.94, and 1.61 ppm decreased. The product as measured from the ratio of the γ-carbon signals was, however, predominantly cis in configuration. At lower temperatures (–45 to –50 °C) and correspondingly longer reaction times, isomerization had still occurred. The *cis*-1-*n*-butylallylsodium produced in this way in THF at –20 °C was therefore cooled to –70 °C, and about 2 mol equiv of butadiene was added to regenerate high fractions of trans allylic structures. When the mixture warmed to temperatures above –55 °C, isomerizations could be measured. Unfortunately some side reaction was also present since a stable end point could not be attained, and a correlation for this slow degradation of the system had to be applied.

No problems exist in the metalation of *trans*-2-heptene by (trimethylsilyl)methylpotassium. The procedures described earlier[2] were followed.

The isomerization rates of the lithium and sodium compounds were measured by use of the difference in near-UV absorptions of cis and trans forms. The latter has always an absorption maximum at longer wavelengths. Concentrations were in the 10^{-2} M region. A Cary 210 spectrophotometer was used, modified so that the cell compartment could accommodate a quartz Dewar vessel provided with optical windows. Methanol was circulated through this vessel at low temperatures from a Haake KT-90 circulating thermostat (or in earlier experiments a Lauda-70 thermostat). Measurements on 1-*n*-butylallylpotassium were made by monitoring the cis and trans γ-proton signals (cis γ, δ 2.47, doublet of triplets, $J_{\beta\gamma}$ = 8.1, $J_{\delta\gamma}$ = 4.5 Hz; trans γ, δ 2.90, doublet of triplets, $J_{\beta\gamma}$ = 13.1, $J_{\delta\gamma}$ = 6.3 Hz). The concentrations used were ~0.5 M; the instrument used was a Varian HA-100 instrument. Temperatures used were calibrated from the frequency difference between proton signals of methanol. Chemical shifts are referenced to the residual α-protons of deuteriotetrahydrofuran as δ 3.58. All preparations and measurements were made in vacuum systems.

Results

The observed rate constants are given in Table I. These are the sum of forward (trans to cis) and reverse constants k_{tc} and k_{ct}.[2] The position of equilibrium must be determined to evaluate the individual rate constants, but since the stable configuration of all the compounds studied is largely cis in THF, k_{tc} is only slightly lower than k_{obsd}. [$k_{tc} = k_{obsd}(K/K + 1)$ where K = [cis]/[trans] at equilibrium]. For the lithium oligomers of butadiene, equilibrium percentages have been given[7] as 83% cis at –40 °C and 66% at 0 °C. Extrapolation to the –60 to –90 °C range used here is not accurate but leads to $K/K + 1$ values in the 0.90–0.96 range. A constant value of 0.93 has been used throughout.

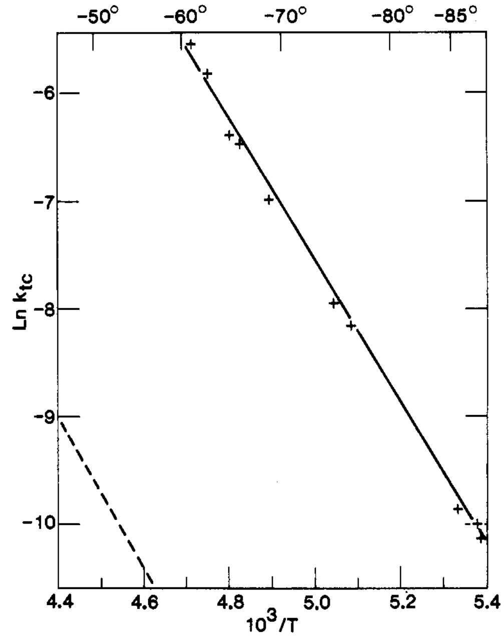

Figure 1. Arrhenius plot of k_{tc} for the isomerization of oligobutadienyllithium in THF. The dashed line indicates the k_{tc} values for neopentylallyllithium. k_{tc} calculated by using $K/K + 1 = 0.93$.

A small change in the equilibrium position of 1-*n*-butylallylsodium was observed between 15 and –18 °C (80% to 85% cis, respectively). A mean value of 0.88 was used at –40 °C for $K/K + 1$ of the sodium oligomer, it being assumed that it had the same equilibrium properties as 1-*n*-butylallylsodium. 1-*n*-Butylallylpotassium was examined over a greater temperature range, 0–80 °C. The cis percentage at equilibrium increased from 80% at 80 °C to 90% at 0 °C. This leads to a mean correction factor of 0.90 over the temperature range used in rate measurements. k_{tc} would of course not be influenced significantly by errors in these estimates but k_{ct} would be rather sensitive to them.

The temperature variation of k_{tc} for the compounds studied is shown in Figures 1 and 2. For comparison purposes, the corresponding data obtained for the neopentyl derivatives are indicated by dashed lines. From Figure 1 it will be seen that the isomerization rates of the oligomeric lithium compound are about 100 times higher than for neopentylallyllithium. This is reflected in the temperature range over which reasonable rates can be measured (–30 to –50 °C for neopentylallyllithium but –60° to –90 °C for the butadiene oligomer). The activation energies are similar, 13.1 kcal mol^{-1} in the present case, 13.$_6$ kcal mol^{-1} for the earlier results on neopentylallyllithium. The uncertainty particularly in the latter case does not warrant any conclusion that they are significantly different. The preexponential factors are, however, very

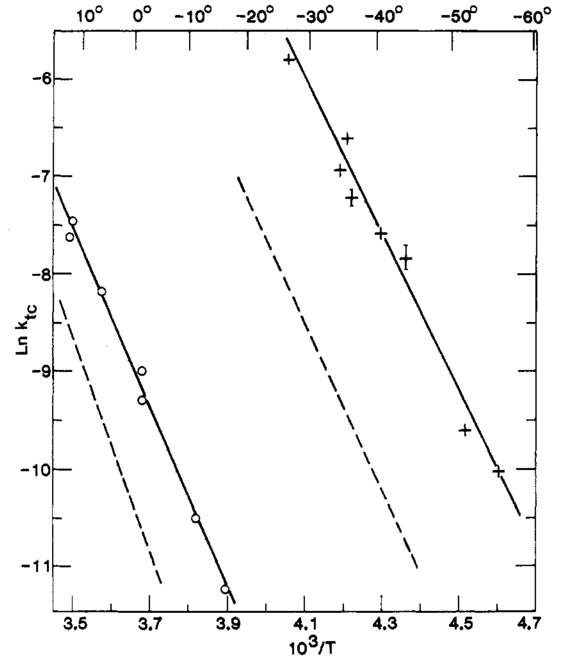

Figure 2. Arrhenius plots of k_{tc} for (+) oligobutadienylsodium and (O) 1-*n*-butylallylpotassium. The dashed line to the left of each indicate the values obtained for neopentylallylsodium and -potassium, respectively. $K/K + 1$ factor used: 0.88 for the sodium compound and 0.9 for the potassium.

different, i.e., ~1 × 10^9 for the neopentyl-substituted compound and 1 × 10^{11} for the longer chain analogue.

The difference in rates is much smaller between neopentylallylsodium and its oligomeric analogue, overall the latter isomerizing about 10 times faster. The activation energy of 16 kcal mol^{-1}, because of corrections for side reactions, has an uncertainty of ±1.5 kcal mol^{-1}, again not experimentally significantly different from that of neopentylallylsodium at $17._1$ kcal mol^{-1}. Isomerization rates become even closer if potassium is the counterion, there being a factor of 2 or less in rates between *n*-butyl- and neopentylallylpotassium. Again as in the other cases, it is the neopentyl derivative which shows the lower rate. The difference in activation energies between the two compounds is in this case significantly larger than the experimental error, i.e., $18._6$ kcal mol^{-1} for the *n*-butyl-substituted compound and $22._2$ kcal mol^{-1} for the neopentyl compound. Simultaneously the preexponential factor has decreased from ~10^{13} to ~10^{11} in the same order. In fact the preexponential factor appears to be ~10^{11} for all three compounds studied in this series but with an activation energy which increases as counterion size increases. The gross overall order of isomerization rates (Li > Na > K) is the same as observed for the neopentylallyl series, with a greater gap in rates between the lithium compound and those of the other alkali metals. In the previous study,[2] the rough parallelism of trans,cis isomerization rates and ease of rotation of the terminal CH_2 group on the anion were noted. This trend, of course, remains in the present series, and the suggestion that both are functions of cation vibrations above the anion plane would still seem to be valid.

The large difference between isomerization rates of the two lithium compounds is notable. It can be determined at least qualitatively that this is not specifically caused by the oligobutadiene chain. 1-*n*-Pentylallyllithium, for example, prepared as described above underwent fast isomerization at −65 °C. The large excess of *n*-butyllithium necessarily present in the sample appears to have little effect on the isomerization rate which although not measured accurately corresponded to a rate constant of 1.1 ± 0.4 × 10^{-3} s^{-1}, only a little lower than that observed for the oligomers in Table I. That neopentylallyllithium shows a distinctly different isomerization rate is illustrated by a modification of the oligomer preparation from *tert*-butyllithium. A reduced (2.4) mol ratio of butadiene was used. Gas chromatographic analysis on the protonated product showed a mixture of 27% neopentylallyl derivative, 39% diadduct, 24% triadduct, and 10% tetraadduct of butadiene. On transfer of the mixture of lithium compounds to THF at low temperature, a fast isomerization reaction was again observed spectrophotometrically at −65 °C. After this had been allowed to proceed until no further change in spectrum was observed, the solution was warmed to −40 °C at which point a second isomerization was observed at a rate close to that expected of neopentylallyllithium. The relative extents were within experimental error equivalent to the amounts of all higher oligomers and neopentylallyllithium, respectively. It appears, therefore, that neopentylallyllithium is abnormal; other allylic lithium compounds have a higher isomerization rate. The same type of effect was, in fact, observed in measurements of isomerization rates in heptane.[5]

The bulky substituent effect is greatly reduced in the allylic compounds of the other alkali metals although there appears to be a general modest increase in isomerization rates on replacement of the neopentyl substituent. This is primarily caused in the case of the two lithium compounds by a large increase in the preexponential factor but smaller decreases in preexponential and activation parameters for the potassium compounds. Errors are large enough in the sodium case to make this type of analysis impossible. It should also be noted that the isomerization rates of the two sodium compounds were measured in quite different concentration ranges, ~10^{-2} M in the present investigation compared to ~0.5 M for neopentylallylsodium. Nevertheless the differences in rates observed are relatively small.

It is interesting to compare the present results with those previously published on ion-pair propagation rates for butadiene in THF[11] and on polymer microstructures.[12] It was observed spectroscopically that trans allylic active centers were kinetically preferred at least for lithium and sodium counterions at low temperatures.[11] At equilibrium, however, the cis structures predominate.[3,4,13,14] Competition between trans,cis isomerization of the active centers and regeneration of the trans forms by monomer addition will occur. Since the activation energies for active center isomerizations found here are always higher than those found for the ion-pair progagation rates, then low temperatures will favor retention of a high trans population as observed previously.

It is obvious also from the present results that in the potassium-based systems, the isomerization rates are so low that relaxation of ion-pair structure will not occur at any practical temperature or monomer concentration. The ion-pair propagation rates are the highest of all the alkali metals studied and the isomerization rates the lowest. The average lifetime of an active center ($1/k_p^{\pm}[M]$) is on the order of a few seconds at −78 °C, dependent on the monomer concentration used, whereas the isomerization half-life must be many hours. At 0 °C owing to side reactions, no reliable rate measurements could be made but $k_p^{\pm}$ is at least 7 M^{-1} s^{-1} which indicates an active center lifetime of at most fractions of a second, whereas the isomerization half-life at this temperature is over an hour. Under these conditions assuming a kinetic preference for trans active centers at all temperatures, the polymer structure should be highly trans in its 1,4 component, as was observed, 84% trans independent of temperature.[12]

Curvature in the Arrhenius plot of rates of butadiene polymerization with sodium as counterion in THF can be interpreted[11] as indicating that the cis,trans population is close to equilibrium at 0 °C and above but out of equilibrium increasingly at lower temperatures. This was at the same time confirmed by observations of the near-UV spectra of the active centers. According to the present results, even at 0 °C equilibration may not be complete at $[M]_0 = 0.2$ M since both the average active center lifetime and the isomerization half-life are about 8 s. Extrapolation errors in k_{tc}, however, introduce some degree of uncertainty in this conclusion. By −30 °C, however, direct measurements are available for both rates. Equilibration of active center isomers is impossible at this temperature, for the isomerization half-life is about $4^1/_2$ min whereas the average active center lifetime is 1–20 s in a normal monomer concentration range. It is not surprising therefore that the 1,4 units in the polymer were found to be virtually all trans in structure at −78 °C with Na^+ as counterion.

In butadiene polymerization with lithium as counterion in THF, trans,cis equilibration is much faster and monomer addition rates slower than with the other counterions. Extrapolation of isomerization rates to 0 °C is sufficiently accurate to give a reasonable estimate of the isomerization half-life as ~0.2 s. At an initial monomer concentration of 0.2 M, the average active center lifetime is 83 s (or 17 s at 1 M monomer). Equilibration will be possible generally at this temperature. At −78 °C the isomerization half-life approaches 1 h. Polymerization rates are very low at this temperature and not measurable with high accuracy. Monomer half-lives will be on the order of several tens of hours at initiator concentrations of 10^{-3}–10^{-2} M. At a conventional range of monomer concentrations (0.2–2 M), the polymerization process appears to be at the critical point where monomer concentration is important. The mean active center lifetime at an average monomer concentration of ~0.7 M was found to be ~0.9 h ($k_p \sim 4 \times 10^{-4}$ M^{-1} s^{-1}), i.e., comparable to the isomerization half-life. The trans content in the 1,4 in-chain structures was, however, already ~90%. These results again are only consistent with a greater reactivity of trans forms.

The measurements of isomerization rates, therefore, confirm generally the scheme suggested previously[9,11] based principally on spectroscopic and polymerization rate data where the sodium counterion was used.

References and Notes

(1) Bywater, S. *Am. Chem. Soc., Symp. Ser.* 1981, *166*, 71.
(2) McDonald, R. T.; Bywater, S. *Organometallics* 1986, *5*, 1529.
(3) Worsfold, D. J.; Bywater, S. *J. Organometal. Chem.* 1978, *159*, 229.
(4) Schlosser, M.; Hartmann, J. *J. Am. Chem. Soc.* 1976, *98*, 4674.
(5) Worsfold, D. J.; Bywater, S. *Macromolecules* 1978, *11*, 582.
(6) Glaze, W. H.; Hanicak, J. E.; Moore M. L.; Chaudhuri, J. *J. Organometal. Chem.* 1972, *44*, 39.
(7) Bywater, S.; Worsfold, D. J.; Hollingsworth, G. *Macromolecules* 1975, *8*, 694.
(8) Glaze, W. H.; Duncan, D. P. *J. Organometal. Chem.* 1975, *99*, 11.
(9) Garton, A.; Bywater, S. *Macromolecules* 1975, *8*, 694.
(10) Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* 1979, *101*, 5459.
(11) Garton, A.; Bywater, S. *Macromolecules* 1975, *8*, 697.
(12) Bywater, S.; Firat, Y.; Black, P. E. *J. Polym. Sci., Polym. Chem. Ed.* 1984, *22*, 669.
(13) Glaze, W. H.; Hanicak, J. E.; Chaudhuri, J.; Moore, M. L.; Duncan, D. P. *J. Organometal. Chem.* 1973, *51*, 13.
(14) O'Brien, D. H.; Russell, C. R.; Hart, A. J. *Tetrahedron Lett.* 1976, 3.

Synthesis of Polyesters Having Pendant Ester Groups by Ring-Opening Polymerization of 4-Methoxycarbonyl-2,6-dioxabicyclo[2.2.2]octan-3-one

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Received September 25, 1986

ABSTRACT: A new polyester (6) having tetrahydropyran rings in the backbone chain and methoxycarbonyl groups as side chains was synthesized by the ring-opening polymerization of 4-methoxycarbonyl-2,6-dioxabicyclo[2.2.2]octan-3-one (5). Monomer 5 was prepared from acrolein and dimethyl malonate via five reaction steps in an overall yield of 23%. Polymerization of 5 was carried out in dichloromethane at −90, −60, and −30 °C with the use of Lewis acid initiators. Soluble polymers having molecular weights up to 1.5×10^5 were obtained with boron trifluoride etherate, whereas a cross-linked polymer was formed with phosphorus pentafluoride. Polyester 6 was soluble in a variety of solvents including chloroform, γ-butyrolactone, acetone, acetonitrile, and dimethyl sulfoxide. It gradually decomposed at 142–152 °C. Copolymerization of 5 with its parent compound 2,6-dioxabicyclo[2.2.2]octan-3-one (1) has revealed that the introduction of a methoxycarbonyl group at the 4-position markedly reduces the polymerizability of the lactone ring. The hydrolysis of films of polyester 6 was examined in 0.001 N hydrochloric acid at 60 °C and compared with that for structurally relevant polyesters 2 and 4.

Introduction

A variety of biologically and biomedically important polymers possessing well-defined heterocyclic structures in their backbones have been produced by ring-opening polymerization of heterobicyclic compounds such as bicyclic acetals, lactones, and lactams.[1-5] Very recently, we synthesized new polyesters 2 and 4 containing tetrahydropyran rings in their main chains by the cationic and

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